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(21) International Application Number: PCT/GB97/01380 (22) International Filing Date: 19 May 1997 (19.05.97) (30) Priority Data: 9610563.0 20 May 1996 (20.05.96) GB (71) Applicants (for all designated States except US): BP CHEMICALS (ADDITIVES) LIMITED [GB/GB]; BP House, Breakspear Way, Hemel Hempstead, Herts HP2 4UL (GB). CASTROL LIMITED [GB/GB]; Burmah Castrol House, Pipers Way, Swindon, Wiltshire SN3 1RE (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): ALLEN, Robert, William [GB/GB]; 32 Callington Road, Saltash, Cornwall PL12 6DY (GB). ATTFIELD, Michael, James [GB/GB]; 13 Earles Meadow, Horsham, West Sussex RH12 4HP (GB). (74) Agent: SMITH, Julian, Philip, Howard; BP International Limited, Group Patents & Agreements, Chertsey Road, Sunbury on Thames, Middlesex TW16 7LN (GB).		(81) Designated States: AU, JP, SG, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: MARINE DIESEL PROCESS AND FUEL THEREFOR (57) Abstract <p>A process for reducing liner lacquering in a marine diesel is described, which process comprises adding to the fuel a liner lacquering reducing amount of a fuel-soluble composition comprising (A) at least one diesel detergent, and (B) at least one combustion improver. The detergent is preferably an imide or amide formed by the reaction of a polyalkene substituted succinic acylating agent and an amine, particularly a succinimide, and the combustion improver is preferably a cerium oxidic compound.</p>		

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MARINE DIESEL PROCESS AND FUEL THEREFOR

The present invention relates in general to marine diesel engines, typically four-stroke medium speed diesel engines, and to fuels therefor. In particular the present invention relates to a process for reducing liner lacquering in a marine diesel engine operating on a fuel capable of giving rise thereto.

5 A problem recently observed in connection with marine diesel engines, such as those powering Dutch fishing vessels, is that of liner lacquering whereby a hard resin-like material forms on cylinder liners and fills the honing grooves. This problem manifests itself in increased lubricating oil consumption which incurs a financial penalty. A solution to the problem, namely replacing the cylinder liners at
10 regular intervals, also carries a financial penalty in that the vessel is temporarily out of commission during replacement of the liners in addition to the cost of replacement itself.

Initially it was thought that the problem was caused by deficiencies in engine design. Later the problem was ascribed to poor lubricating oil quality. The
15 working pattern of the engine and the loads thereon were also thought to be contributory factors. However, a recent paper presented at the 20th International Congress of Combustion Engines, London, 1993, entitled 'The Influence of Marine Fuel Quality On Lubricating Oil Performance' by R W Allen of Castrol International Marine presents a strong case for deteriorating marine diesel fuel
20 quality being a major factor, together with engine overloading, in the occurrence of the problem. The paper makes the observation that gas oil sold into the marine market is in general of lower quality (higher boiling ranges end-point and higher aromatics content) and lower cost than that sold for automotive applications and concludes realistically that even though this type of fuel may be associated with the
25 formation of liner lacquers in overloaded engines it will continue to be produced

and sold because of its lower cost.

Whatever the origins of the problem we have now found that a solution to the problem is to incorporate into the marine diesel fuel certain additives, which hitherto have not been employed as components of marine diesel fuels.

5 Accordingly in one aspect the present invention provides a process for reducing liner lacquering in a marine diesel engine operating on a marine diesel fuel of a quality capable of giving rise to liner lacquering which process comprises adding to the fuel a liner lacquering reducing amount of a fuel-soluble composition comprising:-

- 10 (A) at least one diesel detergent, and
(B) at least one combustion improver.

Marine diesel engines which are prone to liner lacquering problems are generally four stroke engines running on gas oils and to a lesser extent two stroke crosshead engines.

15 Marine diesel fuels of a quality capable of giving rise to liner lacquering are generally those having a high, typically greater than 340°C, for example greater than 360°C, preferably greater than 420°C, temperature for a 90% volume recovery during distillation and a high, ie greater than 25%, particularly greater than 35%, aromatics content. Generally this is accompanied by a low saturates
20 content (less than 60%) and a low olefins content (less than 3%). The cetane number of such fuels is also generally about 40, or less. In addition, marine diesel fuels of a quality capable of giving rise to liner lacquering are generally those of a low sulphur content for example less than 2%, preferably less than 0.5%, more preferably less than 0.2% w/w.

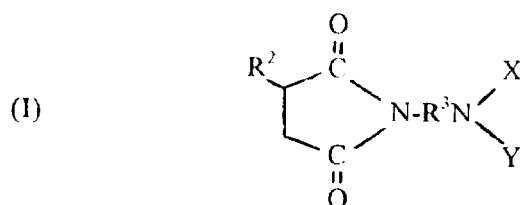
25 The fuel-soluble composition added to the fuel comprises (A) at least one diesel detergent, and (B) at least one combustion improver. As regards the diesel detergent (A), these are materials which function to prevent the build-up of deposits in inter alia the injection system, particularly the injector nozzle, of a diesel engine which can adversely affect both the fuel flow and fuel atomisation
30 characteristics of the injector. The term 'diesel detergent' includes all those materials which would be suitable for use in diesel engines and which have detergent action, generally classified as dispersants which have detergency action. Detergency in diesel engines is generally associated with a range of amine type detergents and polymeric dispersants typified by the following compounds:-
35 amines, imidazolines, amides, fatty acid succinimides, polyalkylene succinimides,

polyalkylene amines and polyether amines. Preferred detergents are (i) oil-soluble amides or imides of long-chain hydrocarbyl-substituted mono- or dicarboxylic acids or their anhydrides and (ii) long-chain hydrocarbons having a polyamine attached directly thereto. A preferred detergent is an imide or amide formed by the reaction
 5 of a polyalkene substituted succinic acylating agent and an amine.

Succinimides are a well-known class of detergent. Typical of the art relating to such materials is GB-A-1565627 and the prior art acknowledged therein. Typically, they are prepared by reacting a polyalkene, in the presence or absence of chlorine, with either maleic acid, or preferably maleic anhydride, to
 10 produce a polyalkene-substituted succinic acid or anhydride and thereafter reacting the polyalkene-substituted succinic acid or anhydride with a nitrogenous material, suitably an amine, which may be a mono-, di- or polyamine.

A suitable succinimide has the formula:-

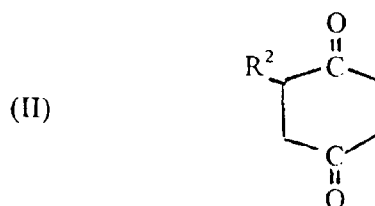
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wherein R² is a hydrocarbyl group, typically a polyolefin group, preferably containing between 30 and 300 carbon atoms, more preferably between 50 and 150 carbon atoms; R³ is a divalent group such that H₂NR³NXY is an alkylene amine, such as an ethylene or propylene amine, for example R³ is -
 25 (CH₂CH₂NH)_kCH₂CH₂ wherein k is zero or an integer from 1 to 7, preferably 2 to 6, or a mixed ethylene/propylene amine, for example H₂N(CH₂)₃NH(CH₂)₂NH(CH₂)₃NH₂; and X and Y are independently either hydrogen, alkyl, or hydroxy alkyl, each of 1-6 carbon atoms, eg methyl, ethyl or hydroxyethyl, or together form the group:-

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Alternatively, R^3 in the formula (I) may be a divalent group such that H_2NR^3NXY is an alkanolamine or a polyether amine. Typically such alkanolamines may contain the group $=N.CH_2CH_2NH.CH_2CH_2OH$ (ie $R^3 = CH_2CH_2$; $X = H$; $Y = CH_2CH_2OH$) and typically such polyether amines may contain the group $=NCH_2CH_2OCH_2CH_2.OCH_2CH_2NH_2$ (ie $R^3 = (CH_2CH_2O)_2CH_2CH_2$; $X = Y = H$). Useful commercially available polyether amines are the Jeffamines (RTM) marketed by Huntsman. R^3 is preferably an alkylene group, eg of 2 to 40 carbon atoms, optionally interrupted with at least one -O- or =NH group and in particular contains one or more units of alkylene oxa or alkylene amino groups, each of 2-4 carbon atoms.

R^3 may also be a divalent group such that H_2NR^3NXY is an aromatic or araliphatic amine, eg of 6-20 carbon atoms, such as phenylene or biphenylene diamine or bis(amino benzyl).

Suitably in the formula (I) R^2 is derived from either ethylene, propylene, 1-butene, isobutene, 1-hexene, 1-octene, and the like. Alternatively, the polyalkene may be derived from an internal olefin, eg 2-butene, or an interpolymers, eg an ethylene/propylene copolymer. Preferably the polyalkene is a polyisobutene.

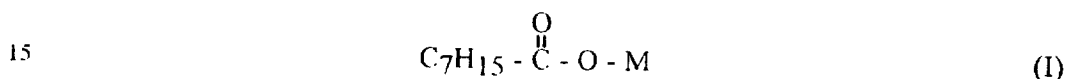
The succinimide may be either a mono- or a bis-succinimide.

Diesel detergents are marketed in various additive packages marketed by several additive manufacturers. In general the additive packages available appear to be based on compounds which can be classified as polymeric dispersants. The high viscosity of these compounds generally dictates that they are distributed in diluted form, typically 50% or more of an aromatic kerosene diluent being used. Any of the commercially available detergents may be employed.

The amount of detergent employed may be sufficient to provide up to 1000 ppm, for example up to 500 ppm, typically up to 250 ppm in the fuel, for example 100 to 200 ppm.

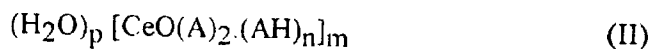
As regards the combustion improver (B), these are compounds which are useful in promoting the combustion of hydrocarbon fuels, in particular diesel fuels. They are believed to act as catalysts for the oxidation of combustion residues and exhaust gases of hydrocarbon fuels. Any of the additives which have been suggested for use in diesel fuels to reduce particulate emissions may be employed as the component (B), for example those described in US Patent Nos. 2,926,454; 3,410,670; 3,413,102; 3,539,312 and 3,499,742. More recently organometallic compounds, either alone or in combination with oxygenated compounds, have been

described as useful for reducing soot and visible particulate matters from the exhausts of diesel fuelled engines. Typical of such combinations are a mixture of an oxygenated compound and an alkyl cyclopentadienyl manganese tricarbonyl as described in US Patent No. 4,207,078; a mixture of a wax oxidate and an
 5 alkylcyclopentadienyl manganese tricarbonyl complex salt as described in US Patent No. 4,222,746; and a mixture of a diesel fuel soluble compound of a rare earth metal, preferably cerium, and an oxygenated compound as described in US Patent No. 4,522,631. Any of the aforesaid combinations may be used in the process of the present invention. As regards the combination of US Patent No.
 10 4,522,631 the diesel fuel soluble compounds of a rare earth metal are suitably organometallic compounds containing oxygen, preferably the carbonyls, typically rare earth metal salts of alkyl carboxylic acids, and of cycloalkyl carboxylic acids, preferably a rare earth octoate of the formula:



where M represents a rare earth metal, preferably cerium. Suitable oxygenated compounds include alkylcarbitols having from about 5 to about 16 carbon atoms, preferably a monoalkyl ether of diethylene glycol. The most preferred carbitol is n-hexylcarbitol.

20 A preferred class of combustion improvers useful in the performance of the present invention are rare earth metal oxidic compounds, preferably cerium oxidic compounds, for example cerium carboxylates, sulphonates, salicylates, and the like. Of the cerium oxidic compounds, preferred compounds include those of Ce(IV), especially those containing for each Ce(IV) atom two residues of an organic
 25 oxyacid, advantageously at least one of which has a pKa greater than 1, or a mixture of such acids, and one other oxygen atom bonded to the Ce(IV) atom in addition to the oxygen atoms constituting the organic oxyacid residues (this oxygen atom being referred to as the "oxidic" oxygen atom). The organic oxyacid may be a carboxylic acid or an organic sulphuric, sulphonic, phosphoric or
 30 phosphonic acid of appropriate pKa. The cerium (IV) oxidic compounds may be represented by the formula:



in which the radicals A, which may be the same or different, are each an anion of an organic oxyacid of the formula AH, p is an integer in the range from 0 to 5,
 35 preferably 4, n is an integer in the range from 0 to 2, preferably either 0 or 2, and m

is an integer in the range from 1 to 12, preferably 6. Examples of suitable compounds embraced within the formula (II) and their preparation are disclosed in US-A-5,449,387, the contents of which are incorporated by reference herein.

Preferred compounds for use in the process of the invention include those
5 derived from cerium and a sulphonic acid.

The amount of combustion improver employed may suitably be sufficient to provide up to 500 ppm, for example up to 200 ppm, typically up to 50 ppm in the fuel; for example from 10 - 50 ppm.

The fuel soluble composition may include as an optional component (C) a
10 cetane improver. These are materials which promote fast oxidation of fuels and thus improve their ignition characteristics. Typical cetane improvers include the alkyl nitrates, ether nitrates, dinitrates of polyethylene glycols and certain peroxides. In general, however, in view of their low cost and ease of handling primary alkyl nitrates are preferred. Examples of suitable cetane improvers useful
15 in the performance of the invention include iso-propyl nitrate, iso-amyl nitrate, iso-hexyl nitrate, cyclohexyl nitrate and iso-octyl nitrate. A preferred cetane improver is iso-octyl nitrate. Desirably the cetane improver should increase the cetane number of the fuel to about 45, or greater.

As a supplement to adding a cetane improver of the aforesaid type the
20 cetane number of the fuel may be increased by the addition of a hydrocarbon fraction known to be beneficial to ignition quality, for example a paraffinic hydrocarbon fraction.

In addition to the components (A) and (B) and optionally (C) the fuel-soluble composition preferably incorporates as component (D) a demulsifier for
25 fuel-water emulsions. Any of the commercially available demulsifiers may be employed, suitably in an amount sufficient to provide a treat level of from 5 to 50 ppm in the fuel. A class of suitable demulsifiers are the quaternary amine salts. Other suitable demulsifiers include alkoxylated polyglycols and arylsulphonates.

The fuel-soluble composition preferably further incorporates as component
30 (E) an antioxidant. Antioxidants are useful for inhibiting gum formation during fuel storage. Diesel antioxidants in current use are mainly based on hindered phenol or amine, for example phenylenediamines, structures. Any of the commercially available diesel antioxidants may be employed, suitably in an amount sufficient to provide a dose rate of from 2 to 200 ppm in the fuel.

35 The fuel-soluble composition may also suitably incorporate a liquid carrier

for the components (A) and (B) and optionally (C), (D) and/or (E). Suitable carriers include liquid hydrocarbons, for example kerosene. Alternatively, diesel fuel itself may be used as a carrier.

5 Additives such as antifoams, for example polysilicone based compounds, corrosion inhibitors, for example carboxylic acids, amines, amides and amine salts of carboxylic acids, wax crystal modifiers/distillate flow improvers, etc., may be incorporated if desired.

The fuel-soluble composition may be incorporated into the fuel during its manufacture.

10 Alternatively the composition may be blended into additive-free fuel contained in the fuel storage tanks of individual vessels.

In another aspect the present invention provides a marine diesel fuel composition suitable for use in a marine diesel engine which composition comprises a marine diesel fuel of a quality capable of giving rise to liner lacquering and a liner
15 lacquering reducing amount of a fuel-soluble composition as hereinbefore described.

A further aspect of the invention comprises the use of a fuel-soluble composition as describe above to reduce liner lacquering in a marine diesel engine.

The invention will now be further illustrated by reference to the following
20 Examples.

Example 1

The lubricating oil consumption of an SWD 240 engine fitted in a Dutch fishing vessel burning an additive-free diesel fuel was measured. A value of 300 litres/week was recorded, which value is consistent with liner lacquering.

25 To the fuel was added a package comprising a polyisobutene succinimide detergent and a combustion improver derived from cerium and a sulphonic acid. The formulation of the package was as follows:

18.8% polyisobutene succinimide
17.1% dodecyl phenol (detergent)
30 5.0% cerium sulphonate (combustion improver)
57.5% solvent
1.2% demulsifier
0.4% antioxidant

The dose was 800 ppm m/m (mg/kg), equating to a level of total detergent in the
35 fuel of about 290ppm, (about 150ppm of succinimide) and a level of combustion

improver of 40ppm.

After an operating period of one month using the fuel containing the package the lubricating oil consumption was again determined. It had fallen to 150 litres/week, thereby demonstrating the effectiveness of the package.

5 **Examples 2-4**

10 The specific lubricating oil consumption of three different engines operating in different vessels under different conditions was evaluated over periods of up to 1200 hours following addition of the additive package used in Example 1. Graphs showing the specific oil consumption as a function of time are shown in Figures 1, 2 and 3. Specific oil consumption is recorded as g/bhp.hr - ie the amount of oil consumed per 1 horsepower of the engine per hour. $1 \text{ g/bhp.hr} = 1.34 \text{ g/kW.hr}$

15 In Example 2 (Figure 1), the dose of package was 650ppm, and it can be seen that by 1000 hours after addition of the package the consumption had fallen from about 1.2 g/bhp.hr to 0.8 g/bhp.hr (1.1g/kW.hr).

20 In Example 3 (Figure 2), the dose of package was 700ppm, and it can be seen that by 1000 hours after addition of the package the consumption had fallen from about 1.1 g/bhp.hr to 0.83 g/bhp.hr (1.1g/kW.hr).

25 In Example 4 (Figure 3), the dose of package was 1200ppm, and 300 hours after addition of the package the consumption had fallen from about 2.2 g/bhp.hr to about 0.8 g/bhp.hr (1.1g/kW.hr).

30 These three results show that for different engines operating under different conditions, the package of the invention is very effective at reducing liner lacquering and hence oil consumption

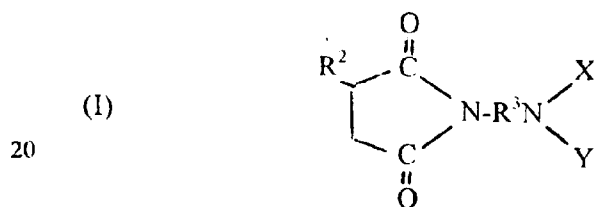
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Claims:

1. A process for reducing liner lacquering in a marine diesel engine operating on a marine diesel fuel of a quality capable of giving rise to liner lacquering, which process comprises adding to the fuel a liner lacquering reducing amount of a fuel-soluble composition comprising:-
 - 5 (A) at least one diesel detergent, and
 - (B) at least one combustion improver.
2. Process according to claim 1 wherein the detergent is (i) an oil-soluble amide or imide of a long-chain hydrocarbyl-substituted mono- or dicarboxylic acid or its anhydride, or (ii) a long-chain hydrocarbon having a polyamine attached
 10 directly thereto.
3. Process according to claim 2 wherein the detergent is an imide or amide formed by the reaction of a polyalkene substituted succinic acylating agent and an amine.
4. Process according to claim 3 wherein the detergent is a succinimide of the
 15 formula

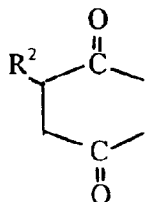


wherein R^2 is a hydrocarbyl group, preferably a polyolefin group; R^3 is a divalent group such that H_2NR^3NXY is an alkylene amine, preferably an ethylene or
 25 propylene amine, or R^3 is a divalent group such that H_2NR^3NXY is an

alkanolamine, a polyether amine, or an aromatic or arylaliphatic amine; and X and Y are independently either hydrogen, alkyl, or hydroxy alkyl, each of 1-6 carbon atoms, preferably methyl, ethyl or hydroxyethyl, or together form the group:-

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(II)



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5. Process according to claim 4 wherein in the succinimide detergent of formula (I), R^2 is a polyolefin group containing from 30 to 300 carbon atoms, preferably from 50 to 150 carbon atoms; and R^3 is $-(CH_2CH_2NH)_kCH_2CH_2$

15 wherein k is zero or an integer from 1 to 7, preferably 2 to 6, or a mixed ethylene/propylene amine, preferably $H_2N(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$.

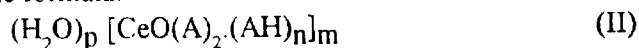
6. Process according to claim 4 wherein H_2NR^3NXY is an alkanolamine or a polyether amine, and the alkanolamine contains the group $=N.CH_2CH_2NH.CH_2CH_2OH$ (ie $R^3 = CH_2CH_2$; $X = H$; $Y = CH_2CH_2OH$) and the polyether amine contains the group $=NCH_2CH_2OCH_2CH_2.OCH_2CH_2NH_2$ (ie $R^3 = (CH_2CH_2O)_2CH_2CH_2$; $X = Y = H$).

20

7. Process according to claim 4, 5 or 6 wherein R^2 is derived from ethylene, propylene, 1-butene, isobutene, 1-hexene, 1-octene, 2-butene, or an ethylene/propylene copolymer, and is preferably a polyisobutene.

8. Process according to any preceding claim, wherein the combustion improver is a rare earth metal oxidic compound, preferably a cerium oxidic compound, more preferably a cerium carboxylate, sulphonate or salicylate.

9. Process according to claim 8 wherein the combustion improver is a cerium (IV) oxidic compound of the formula:



30 in which the radicals A, which may be the same or different, are each an anion of an organic oxyacid of the formula AH, p is an integer in the range from 0 to 5, preferably 4, n is an integer in the range from 0 to 2, preferably either 0 or 2, and m is an integer in the range from 1 to 12, preferably 6.

10. Process according to any preceding claim, wherein the amount of detergent employed is such as to give a level of detergent in the fuel of up to 1000ppm,

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preferably up to 500ppm, and more preferably from 100 to 200ppm.

11. Process according to any preceding claim, wherein the amount of combustion improver employed is such as to give a level in the fuel of up to 500ppm, preferably up to 200ppm, and more preferably up to 50ppm.

5 12. Process according to any preceding claim wherein the fuel-soluble composition additionally comprises (C) a cetane improver, which is preferably an alkyl nitrate, ether nitrate, dinitrate of a polyethylene glycol or a peroxide; and/or (D) a demulsifier for fuel-water emulsions; and/or (E) an antioxidant.

10 13. Process according to any preceding claim wherein the marine diesel fuel has a 90% volume recovery during distillation at a temperature greater than 340°C, preferably greater than 360°C, and more preferably greater than 420°C; and/or an aromatics content greater than 25%, preferably greater than 35%; and/or a saturates content of less than 60% and an olefins content of less than 3%; and/or a cetane number of 40 or less; and/or a sulphur content of less than 2%, preferably
15 less than 0.5%, more preferably less than 0.2% w/w.

14. A marine diesel fuel composition suitable for use in a marine diesel engine, which composition comprises a marine diesel fuel of a quality capable of giving rise to liner lacquering and a liner lacquering reducing amount of a fuel-soluble composition as defined in any preceding claim.

20 15. Use of a fuel-soluble composition as defined in any of claims 1 to 13 to reduce liner lacquering in a marine diesel engine.

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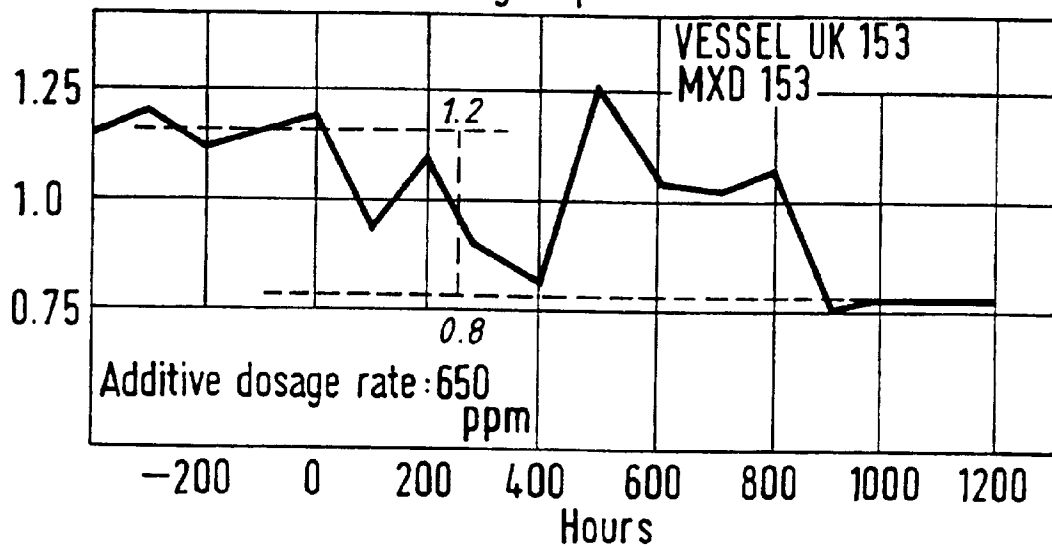
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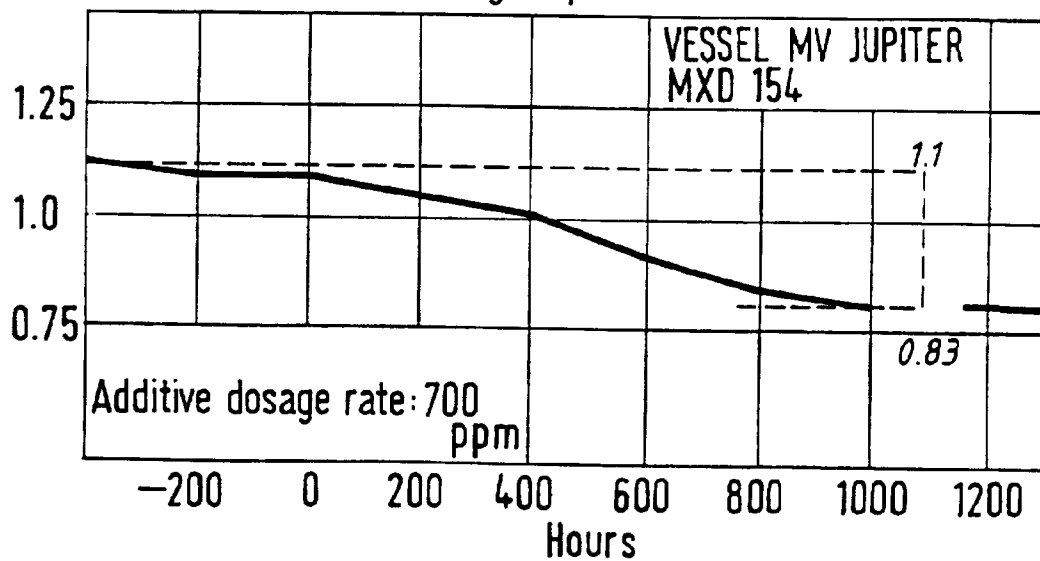
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FIG. 1

SPECIFIC OIL CONSUMPTION. g/bhp.hr

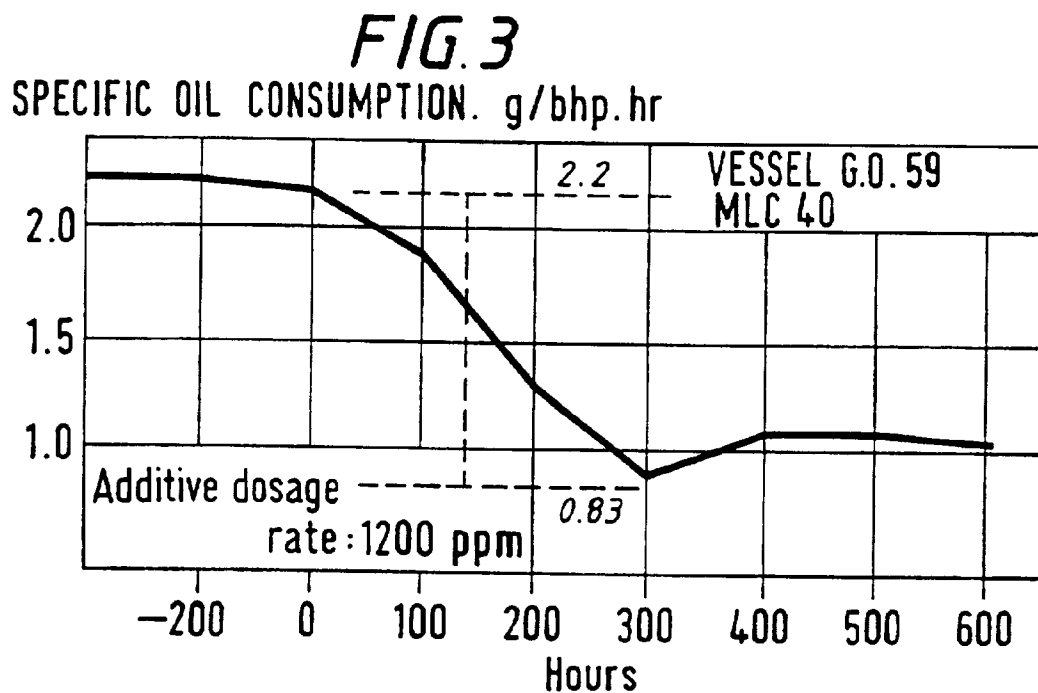
**FIG. 2**

SPECIFIC OIL CONSUMPTION. g/bhp.hr



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INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 97/01380

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C10L1/14 C10L10/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,Y	WO 96 15209 A (BP) 23 May 1996 see the whole document ---	1-15
P,Y	WO 96 26255 A (RHONE-POULENC) 29 August 1996 see the whole document ---	1-15
Y	EP 0 575 189 A (RHONE-POULENC) 22 December 1993 cited in the application see the whole document ---	1-15
X	EP 0 423 744 A (LUBRIZOL) 24 April 1991 see abstract; claims 65,71,73,74 --- -/--	1-8,10, 11,14,15

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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